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Thermochemical Hydrogen Cycle

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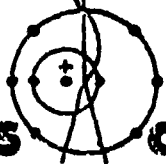
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PROCESS DESIGN OF THE LASL BISMUTH SULFATE THERMOCHEMICAL HYDROGEN CYCLE

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ABSTRACT

A new process engineering flowsheet reflecting an improved design of the LASL Bismuth Sulfate thermochemical cycle is presented. The design is based on laboratory data that indicate a lowered endothermic heat load for a partial decomposition of the solid bismuth sulfate. A small electrical energy demand should result from operation of the sulfur dioxide electrolytic step at lower acid concentration, in principle. The results of the flowsheeting analysis yield a thermal efficiency of 50 percent for the cycle when coupled to a conceptual fusion energy heat source at 1500 K. A parametric analysis shows a slight drop in efficiency as the temperature of the heat source is decreased. The LASL Bismuth Sulfate thermochemical cycle appears to have potential as a means of producing hydrogen from high-temperature heat sources such as fusion, fission, and solar energy; it also appears to be competitive with alternative thermochemical cycles as well as with water electrolysis for hydrogen production.

THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION have been investigated at the Los Alamos Scientific Laboratory (LASL) since the early 1970's. These studies have consisted of experimental and engineering research to define practical cycles that can be coupled to high-temperature heat sources for water-splitting to produce hydrogen and oxygen. Sponsorship of these programs has been obtained from DOE's Division of Basic Energy Sciences and Energy Storage Systems. In recent months, our efforts have concentrated on the development of a thermochemical cycle that is compatible with a 1500 K temperature heat source derived from a conceptual fusion driver. This study, mainly sponsored by DOE's Office of Fusion Energy has as its major goal the task of defining nonelectrical fusion energy applications. Chief among these applications has been the study of synfuel (hydrogen) production from fusion power, the results of which are discussed elsewhere at this Conference. (1)*

This paper addresses the status of the chemical process design of the thermochemical cycle chosen for coupling to the fusion driver. In selecting a specific thermochemical cycle for this study the following ground rules were adopted.

CHEMISTRY

- o The cycle should have some basis in experimental fact.
- o Thermodynamic data should be available.
- o Kinetic data on the important reactions should exist.

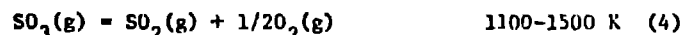
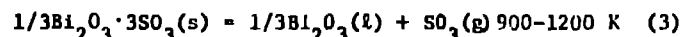
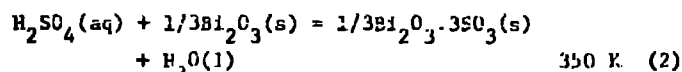
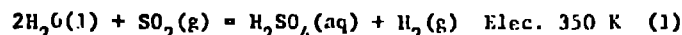
ENGINEERING

- o Cycle energy requirement characteristics should match the thermal energy source.
- o Cycle should avoid highly corrosive environments wherever possible.
- o Heat exchange should be minimized.

With these considerations in mind, a "hybrid" bismuth sulfate thermochemical cycle under development at LASL was selected for study. (A "hybrid" cycle is one which operates partly on thermal energy and partly on "work" energy, i.e., a low-temperature electrolysis step is incorporated within the cycle).

THE LASL BISMUTH SULFATE CYCLE

The reference bismuth sulfate cycle has already been analyzed elsewhere (2); however, it is useful to review its chemistry as an aid towards understanding the present version of the cycle. The reference cycle consists of the following steps:



This cycle was originally devised as an alternative to those cycles that employ sulfuric acid as one of their reactants. In these cycles, sulfuric acid is present in solution at around 50 wt% concentration. These solutions are concentrated by evaporation to the azeotropic concentration at around 98 wt% acid prior to sulfuric acid decomposition to water, sulfur dioxide and oxygen. Serious materials problems are experienced in the evaporation process due to the highly corrosive nature of boiling sulfuric acid solutions. In addition large heat penalties may be incurred unless multiple effect evaporation which involves expensive capital equipment is invoked. Among the cycles employing sulfuric acid processing are the hybrid sulfur cycle under development by Westinghouse, (3) the General Atomic sulfur-iodine cycle, (4) and the Mark-13 sulfuric acid-bromine cycle being studied at the Euratom Center, Ispra, Italy. (5) These three cycles have passed the laboratory stage of development and are being studied in bench-scale apparatus capable of continuous operation to produce 100 liters of hydrogen per hour. Much attention is being devoted to the aforementioned materials problem.

At the LASL, we have sought to avoid hot concentrated sulfuric acid corrosion and drying problems by precipitating an insoluble, anhydrous metal sulfate from the sulfuric acid solution as shown in step 2, above. The bismuth system was selected on the basis of the formation of insoluble, anhydrous bismuth sulfate on precipitation. Additional heat would be required in the cycle if hydrated sulfate species were formed, as in the case of copper sulfate, say. In step 2 of our reference cycle, bismuth oxide is added to sulfuric acid having a concentration greater than or equal to 52.7 wt% to form the normal bismuth sulfate, (6) this sulfate after drying can be decomposed thermally to bismuth oxide and sulfur trioxide as shown in step 3. Sulfur trioxide further decomposes to sulfur dioxide and oxygen which are separated to provide recycle sulfur dioxide for step 1, the electrochemical oxidation of sulfur dioxide to sulfate.

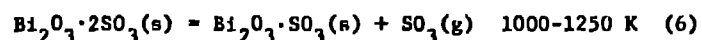
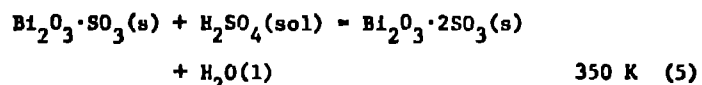
*Numbers in parentheses designate References at the end of paper.

acid and hydrogen product. The electrochemical oxidation of sulfur dioxide to give hydrogen is the "hybrid" step in this process; this reaction was first investigated by Bowman and Onstott at the LASL,(7) and is a key step in the Westinghouse cycle.(3) Comparison of the steps in the LASL Bismuth Sulfate cycle to other cycles shows that solid materials must be handled. Traditionally, solids are avoided in favor of liquids and gases because of handling problems. The trade-off must be made between solids handling and the difficulties (and expense) of handling highly-corrosive boiling sulfuric acid streams. This is a future direction of our proposed research.

CYCLE VARIATIONS

Variations in the reference bismuth sulfate cycle are possible as a result of the existence of a set of intermediate bismuth oxysulfate compounds that result when normal bismuth sulfate, $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$, decomposes to bismuth oxide, Bi_2O_3 . This is illustrated in Fig. 1 which also indicates approximate temperatures at which the transformations take place. In the reference design, we considered the removal of one mol of SO_3 from 1/3 mol of the normal bismuth sulfate to yield 1/3 mol of bismuth oxide (step 3). The endothermic heat requirement was taken as 251 kJ/mol SO_3 from tabulated thermodynamic data.(8) At the decomposition temperatures chosen, the bismuth oxide formed is in the liquid state complicating the design of the decomposition reactors.(9) Recuperation of normal bismuth sulfate also required reasonably high acid concentration (52.7 wt% or higher) which in turn indicated an electrolyzer voltage of 0.6 V or higher. Our preliminary assessment of the reference cycle's efficiency was 41% on these bases.

To optimize cycle performance, primarily in the area of efficiency improvement, cycle variations were devised that were based on the effect of cycling between two of the intermediate bismuth oxysulfate compounds in the decomposition sequence shown in Fig. 1. An improved cycle would operate between the compounds, $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ and $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$. Experimental data on the endothermic heat of decomposition of $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ are presented in Table 1. Steps 2 and 3 presented for the reference cycle would be replaced by the following two steps:

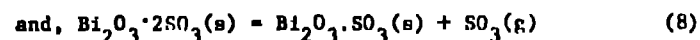
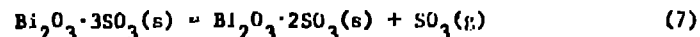


The improved cycle is shown in schematic form in Fig. 2. There are several advantages with this variation:

- o The average endothermic heat requirement for the solid decomposition step would decrease from 251 kJ/mol to 172 kJ/mol SO_3 removed.
- o $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ is the stable solid phase in contact with sulfuric acid over a 3 wt% to 52.7 wt% concentration range;(6) in principle, the electrochemical oxidation of sulfur dioxide (step 1) could be carried out at a voltage lower than 0.6 V due to a reduction in the theoretical voltage as well as a possible reduction in over-voltage. Operation in the 10-20 wt% sulfuric acid range would be feasible.
- o Sulfuric acid is not handled at high concentrations or temperatures.
- o Both sulfates present in step 6 would remain in the solid phase throughout the reaction avoiding difficult to contain molten oxide.
- o Maximum temperatures required for solids decomposition can be lower.

A second alternative would involve decomposition of $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to a stage represented by $\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3$. As opposed to these advantages, the only foreseeable disadvantages would be the circulation of a larger amount of solid, one mol of bismuth oxysulfate per mol of sulfur trioxide removed with attendant increased liquid entrainment, and a higher circulation rate for the sulfuric acid electrolyte in the sulfur dioxide electrolyzer.

CYCLE EXPERIMENTAL VERIFICATION - The experimental bases for the above observations are shown in Figs. 3 and 4. Thermodynamic data on the endothermic heat of reaction for:



were obtained in isothermal batch experiments. The SO_3 pressure was obtained from total ($\text{SO}_3/\text{SO}_2/\text{O}_2$) pressure measurements over samples of bismuth oxysulfate of known composition as a function of temperature. Straight line plots of $\log P_{\text{SO}_3}$ vs. $1/T$ gave a value of 161 kJ/mol (38.4 kcal/mol) for the $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ decomposition and 172 kJ/mol (41.2 kcal/mol) for the $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ decomposition respectively. These data and the experimental plots are shown on Fig. 3.

Table 1 - Bismuth Sulfate Decomposition Data

Reaction	T, K ($P_{\text{SO}_3} = 1 \text{ atm}$)	ΔH , kJ/mol SO_3	H_2SO_4 , wt% in eq. with reactant (6)
$\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 + \text{SO}_3$	876	161	52.7 +
$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 = \text{Bi}_2\text{O}_3 \cdot \text{SO}_3 + \text{SO}_3$	1121	172	3.0 - 52.7
$\text{Bi}_2\text{O}_3 \cdot \text{SO}_3 = \text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3 + 1/3\text{SO}_3$	1253 +	-	< 3.0
$\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3 = \text{Bi}_2\text{O}_3 + 2/3\text{SO}_3$	1293 +	-	-
Overall			
$\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Bi}_2\text{O}_3 + 3\text{SO}_3$	876	786 (8)	52.7 +

Kinetic data for the decomposition of $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ starting material are shown in Fig. 4. Isothermal runs were performed by dropping a small sample of normal bismuth sulfate into a preheated furnace. The sample came to within two degrees of the furnace temperature in about two minutes. The plots in Fig. 4 show the rate of SO_3 removal as a function of time at temperatures of 1048, 1153, and 1243 K. In all cases after long enough times (30 + minutes), the normal bismuth sulfate decomposed to yield a solid material with the approximate stoichiometric formula of $\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3$ releasing 2.33 mols of SO_3 . The decomposition times for the release of 2 mols of SO_3 (to form $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$) is dependent on the run temperature. About 1.5 min is required for the decomposition of $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ to $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ at 1243 K. Less time (roughly half) would be required for the intermediate step, $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$. In these experiments it is very probable that the reaction rate is determined by temperature-dependent kinetics rather than by heat transfer. In large industrial reactors, heat transfer may play a larger role depending on particle size, etc. In one chosen contacting scheme, i.e., fluidized beds, heat and mass transfer rates are large and thus reaction times would be temperature-dependent. In an actual process, solid material corresponding to $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ or $\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3$ would be removed from the decomposition reactor for contact with 10-20 wt% acid from the electrolyzers to produce $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ starting material. For simplicity, we have considered only removing SO_3 as far as $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ in the optimized design. Again, in an actual process, the starting material would be slightly more enriched in SO_3 than suggested by $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ as a result of reaction between the sulfuric acid present in the liquid (that is removed by drying) occluded by the $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ precipitate.

We are presently exploring continuous methods to decompose $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$. Several solid handling approaches suggest themselves, these include: fluidized beds, rotary kilns and vertical moving beds. We have begun testing of the fluidized bed alternative and have found a major variable to be the physical aspect of the solid sulfate material (particle size and shape, particle size distribution, tendency to agglomerate or "pill," etc.).

CYCLE PROCESS DESIGN

A thermochemical process design has been developed for the reference as well as for the improved version of the LASL Bismuth Sulfate cycle. The design aims were to produce an engineering flowsheet, compute mass and energy balances, and obtain a value for the thermal efficiency of the cycle. The eventual aim is to obtain the cost of hydrogen production. For ease of analysis, the cycle was split into two portions, a portion involving the low-temperature operations and a high-temperature portion. The flowsheet for the low-temperature part is shown on Fig. 5, with the high-temperature part's flowsheet being shown on Fig. 6.

A fusion reactor deposits neutrons in a high-temperature boiling lithium blanket at 1500 K. Thermal energy from the isothermal "lithium boiler" (10) is transferred directly to a $\text{SO}_3/\text{SO}_2/\text{O}_2$ process stream for the high-temperature portion of the cycle. One heat exchanger thus provides all the primary thermal energy for the cycle. Heat from a low-temperature (800 K) portion of the fusion blanket provides the energy for electric power generation for the electrolysis section located in the low-temperature portion of the cycle. We have assumed equilibrium compositions in all gas streams containing $\text{SO}_3/\text{SO}_2/\text{O}_2$ except after rapid quenching to temperatures below 800 K. Data for this equilibrium were obtained from thermodynamic compilations. (11) For pipeline service, hydrogen is required at pressures substantially above atmospheric

pressure. We have chosen a design pressure of 3 MPa (30 atm.) as the operating pressure in the electrolyzer vessel to yield a hydrogen product at this pressure for outside delivery and the same pressure in the decomposition reactors to minimize their size. In this design, we have also assumed negligible thermal and pumping (transfer) losses in comparison with the thermal energy flows. The high-temperature decomposers are thus designed to operate isobarically neglecting for the time being pressure drops through the reactors. Inclusion of these factors would make minor downward adjustments to the calculated estimate of the cycle's efficiency.

CYCLE-LOW TEMPERATURE PORTION - Three major components of the process are included in the low-temperature portion. These components are: the sulfur dioxide oxidation electrolyzers, the bismuth oxysulfate precipitation reactors, and the units for separating SO_2 from O_2 and the extraction of energy from the oxygen stream by expansion to ambient conditions. This portion of the cycle is illustrated in Fig. 5. In the electrolytic step (7), sulfurous acid is oxidized with the simultaneous formation of hydrogen at the cathode. Migration of sulfurous acid to and subsequent formation of sulfur at the cathode must be avoided. This problem was first overcome by the provision of a slight catholyte over-pressure in conjunction with a suitable porous membrane. In our design, we have assumed slightly semi-permeable, ion-conducting membrane that reduces sulfurous acid migration into the cathode compartment of the electrolytic cell. The electrolytic cell design parameters have been chosen at: Cell Voltage: 0.45 V, Current Density: 2000 A/m², Temperature: 350 K, Pressure: 3MPa (30 atm.), and Acid Concentration: 10-20 wt%. Experiments are being pursued at this time to verify the choice of these operating parameters for the electrolysis portion of the cycle. The effluent acid stream at 20 wt% is cooled by heat exchange prior to being reacted with the bismuth oxysulfate ($\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$) effluent from the decomposer vessels. These reactors produce a wet $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ precipitate that is returned to the high-temperature portion of the cycle. Some heat is liberated at low temperature in the reaction of $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ with sulfuric acid. We estimate this amount of heat to be 38 kJ/mol which is roughly half the heat release for the reaction of bismuth oxide with sulfuric acid to form $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$. This heat serves to raise the temperature of the acid effluent from the bismuth oxysulfate reactors. The acid effluent is then introduced into a series of gas absorbers where it is used to separate SO_2 from the SO_2/O_2 stream leaving the decomposers. This operation recovers SO_2 which is then recycled with the acid back to the electrolyzers. The oxygen stream from the absorbers contains trace amounts of SO_2 which is further reduced by contact with the incoming water to the cycle. After final scrubbing, the oxygen stream is heated, expanded to recover useful work, and vented at close to ambient conditions to the atmosphere.

It is of interest to note other proposed SO_2/O_2 separation schemes that depend on the cryogenic separation of SO_2 by its liquefaction from non-condensable oxygen (at the specified temperatures). These schemes may be flawed as oxygen possesses a considerable solubility in liquid SO_2 . (12) The temperature coefficient of solubility for oxygen is positive, thus the liquid SO_2 must be at an even lower temperature for greater oxygen removal.

CYCLE-HIGH TEMPERATURE PORTION - This portion of the cycle includes the bismuth sulfate drying step, the bismuth sulfate decomposition, and the sulfur trioxide decomposition steps. Isothermal energy at 1500 K from condensing lithium vapor supplies heat to the high-temperature portion of the cycle by driving the equilibrium reaction: $\text{SO}_3 = \text{SO}_2 + 1/2\text{O}_2$ to the right. The shift of the equilibrium to the left when the gas

mixture drops to lower temperature gives a heat evolution that is used for the endothermic decomposition of entering $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ in a "chemical heat pipe" mechanism. In this manner, primary heat from the fusion reactor is coupled to this portion of the cycle in a single heat exchanger. The other heat exchangers shown on the flow-sheet, Fig. 6, are for internal heat recovery, i.e., preheating incoming "cold" streams with exiting "hot" streams.

The equilibrium pressures for the $\text{SO}_3/\text{SO}_2/\text{O}_2$ system are well known (11) and data for this system, in the form of P_{SO_3} , has been plotted as a function of temperature at a total pressure of 3 MPa (30 atm.) on Fig. 3. We see that the crossover point with the $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ decomposition line occurs at 1251 K. Above this temperature SO_3 obtained from the decomposing bismuth oxy-sulfate will equilibrate with SO_2 and O_2 . The corresponding temperature for the $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ decomposition is 1010 K.

With reference to the flowsheet, Fig. 6, entering $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ mechanically "dewatered" to 87 wt% solids containing roughly 5 mols of water per mol of entering solid is dried by indirect contact with a warmer stream of quenched $\text{SO}_2/\text{O}_2/\text{SO}_3$ containing the evaporated water. Additional heating is provided by an internal recycle stream of oxygen. Leaving the bottom of the drier, we have a vapor stream composed mainly of SO_2 and O_2 and a liquid stream containing water and sulfuric acid. The dry solids exit the top of the drier vessel where they contact directly a quenched $\text{SO}_2/\text{O}_2/\text{SO}_3$ stream that comes directly from the SO_3 decomposer (primary heat exchanger) and is essentially unchanged in composition from its equilibrium at 1500 K at 3 MPa (30 atm.). Heat exchange occurs between these streams raising the temperature of the dried $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to approximately 800 K. Additional heat to raise the temperature of the solids is obtained from a recycle $\text{SO}_2/\text{O}_2/\text{SO}_3$ stream as well as from the recycle oxygen. The dried and heated $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ solids are now introduced into a series of decomposition reactors (two are shown on Fig. 6) where they come into direct contact with a $\text{SO}_2/\text{O}_2/\text{SO}_3$ gas mixture from the primary heat exchanger. We have assumed equilibrium conditions at the inlet and outlet temperatures of these decomposer vessels for the gas phase. In the decomposers, the solids are heated by two mechanisms, sensible heat exchange with the hotter gases and by the heat of reaction given up as some of the SO_2 and O_2 present shifts towards SO_3 . This forms the heat recovery portion of the chemical heat pipe mechanism described earlier. This process drastically reduces the gas flows from what they would have to be if only sensible heat were exchanged. As stated earlier, the decomposition reactors are solid-gas contacting devices. These units could have several configurations: fluidized beds, moving beds, or rotary kilns, etc. Criteria for decomposer reactor design would include considerations of temperature, pressure, reaction rate and heat transfer. Some thought has also been given to the possibility of the solids themselves acting as catalytic surfaces for the $\text{SO}_2/\text{O}_2/\text{SO}_3$ equilibrium. Should the solid material prove to be catalytically inactive, catalyst coatings on interior surfaces of the decomposer vessels may have to be provided.

In our design, we have considered the removal of 1 mol of SO_3 per mol of entering $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ as well as the removal of 1.33 mols of SO_3 to yield a product of $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ or $\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3$ respectively. The exiting solid material is cooled by the internally recycling oxygen stream before its discharge. This material is returned to the low-temperature portion of the cycle for subsequent contact with sulfuric acid and regeneration to the $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ starting material.

CYCLE-ENERGY BALANCE AND EFFICIENCY - In order to obtain quantitative data for the performance of this

cycle relative to other cycles and to water electrolysis, we have done parametric analyses of the cycle's energy balance over a wide range of operating conditions.

High-temperature Portion of the Cycle - An enthalpy balance model illustrated in Fig. 7 was constructed to obtain the endothermic heat per mol of H_2 , Q_H , required in the high temperature portion. We have assumed negligible heat losses and a 25 K temperature difference for heat transfer in this portion. The endothermic heat requirement may be expressed as:

$$Q_H = \sum_{\text{in}} n_i h_i (350 \text{ K}) - \sum_{\text{out}} n_j h_j (375 \text{ K}) \quad (9)$$

where, n_i = mols component i , and h_i = molar enthalpy of components.

The variables explored and their ranges were:

Maximum Stream Temperature: 1275-1675 K

System Pressure: 2 MPa (20 atm.) - 5 MPa (50 atm.)

Mols SO_3 Removed: 1.0 and 1.33

Mols H_2O entering with $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$: 0-20

(as 15 wt% H_2SO_4)

Fig. 8 shows the results of one of the evaluations in which the variation of Q_H is plotted against the entering moles of water as a function of maximum temperature and the number of mols of SO_3 removed. We note a minima in the curves resulting from two effects: a) the 25 K temperature difference between the feed and outlet streams, and b) the recombination of unreacted SO_3 that combines with water in the outlet stream to form H_2SO_4 , releasing about 289 kJ/mol as heat of reaction and liquid solution formation. Less endothermic heat is required for $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ transforming to $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ rather than to $\text{Bi}_2\text{O}_3 \cdot (2/3)\text{SO}_3$; however, this may be balanced against a small increase in materials circulation.

For a representative energy balance and efficiency calculation, the following process conditions were chosen: Max. Temp.: 1475 K, Press.: 30 atm., Mols SO_2 removed: 1.0, and Mols H_2O entering: 5.0. The overall energy balance for the cycle is given in Table 2 below for these conditions.

Table 2 - Cycle Energy Balance

Process Step	Heat Required kJ/mol H_2	Heat Available kJ/mol H_2	Work (Heat Equiv.) kJ/mol H_2
High Temperature Portion	285		
Low Temperature Portion			
a. Electrolyzer			226 ^a
b. $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ Formation Reactor		(38) ^b	
c. SO_2/O_2 Separator	20	14	54 ^a
	305	14	282

^a Heat to work conversion @ 39%

^b Heat at 350 K

The cycle efficiency η is: $\Delta H_{H_2}/EQ_{TOT}$. In our case we have

$$\eta = \frac{286}{305 + 282 - 14} = 0.50 \text{ (50\%)}$$

A further parametric analysis was done to evaluate the effect of the major system variables on the cycle's efficiency. Three variables were chosen for this analysis; the electrolyzer cell voltage, the endothermic heat requirement in the high-temperature portion, and the maximum stream temperature in the cycle. Held constant were the system pressure at 3 MPa, the mols of SO_3 removed at 1.0, and the mols of water entering the high-temperature portion at 5.0. The results of this further analysis are shown on Fig. 9. In the case of the variation of cell voltage, the temperature was kept constant at 1475 K, and the endothermic heat at 285 kJ/mol H_2 . In the other two cases considered, the cell voltage was kept at 0.45 V (228 kJ/mol, heat equivalent).

The results show that the most important variables bearing on the cycle's efficiency are the electrolyzer voltage and the endothermic heat requirement. The effect of maximum stream temperature variation is important primarily because it varies the equilibrium yield in the $SO_3 = SO_2 + 1/2 O_2$ reaction and hence changes the composition of the gas mixture leaving the high-temperature portion of the cycle and the endothermic heat requirement.

Our earlier look at the variation in overall system pressure showed small changes in Q_H with pressure over the range 20-50 atm and thus not much variation from the point of efficiency. The major effect of varying system pressure in a gaseous system would be to change equipment sizes and structural requirements thus influencing the capital costs of the cycle.

To obtain a cycle with high overall thermal efficiency, it is important to choose operating conditions that minimize thermal energy expenditure. In the case of the bismuth sulfate cycle, these conditions are fulfilled by the choice of a reasonably high maximum stream temperature (1475 K), high system pressure (3 MPa), low electrolyzer voltage (0.45 V), 1 mol of SO_3 removed per entering $Bi_2O_3 \cdot 2SO_3$, and a low number of mols of water entering the high-temperature portion of the cycle (< 5 mols).

MATERIALS - Materials problems must be faced in designing a thermochemical cycle for operation at temperatures around 1500 K. The principal choice of materials in the low-temperature portion of the cycle for components in contact with 350-400 K H_2SO_4 would be plastic-lined steel. At temperatures from 400-800 K an acid brick may be used to line equipment. For the high-temperature portion of the cycle we have to contain bismuth oxysulfates as well as dry SO_3 , SO_2 , and O_2 . The high-temperature form of SiO_2 or a recently announced oxidation resistant SiC sponge (13) have capabilities to 1800 K. These problems, however, will require more detailed investigation.

SUMMARY AND CONCLUSIONS - The LASL bismuth cycle appears to be a promising approach to producing hydrogen from a high-temperature process heat source (1500 K) such as that from a fusion or solar reactor. It avoids the problem of evaporating sulfuric acid solutions and has an estimated efficiency of 50 percent based on a flowsheet analysis. Crucial issues still to be resolved for this cycle are the demonstration of low voltage electrolysis under production conditions, recuperation of latent heat of vaporization from drying solid $Bi_2O_3 \cdot 2SO_3$, and the handling of large amounts of solids in a high-temperature decomposer vessel.

We have not evaluated the cycle on economic grounds as yet, however, similarity of the cycle to other cycles undergoing techno-economic evaluation other than for solids handling equipment indicate that the hydrogen production cost should be roughly comparable.

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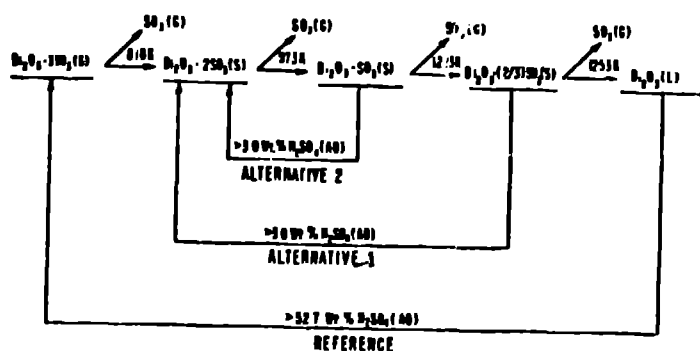


Fig. 1. Bismuth Sulfate Decomposition Alternatives

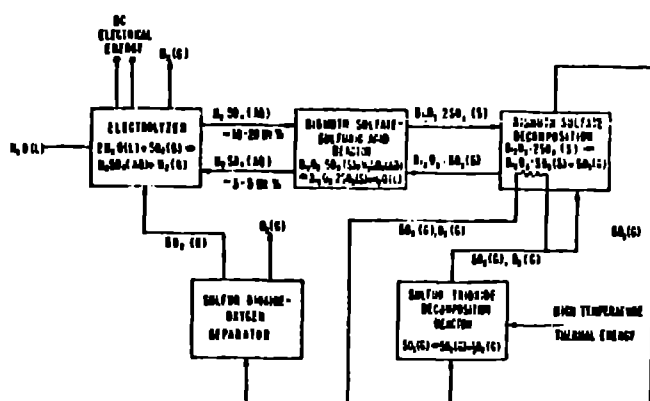


Fig. 2. Schematic Diagram of the LASL Bismuth Sulfate Cycle.

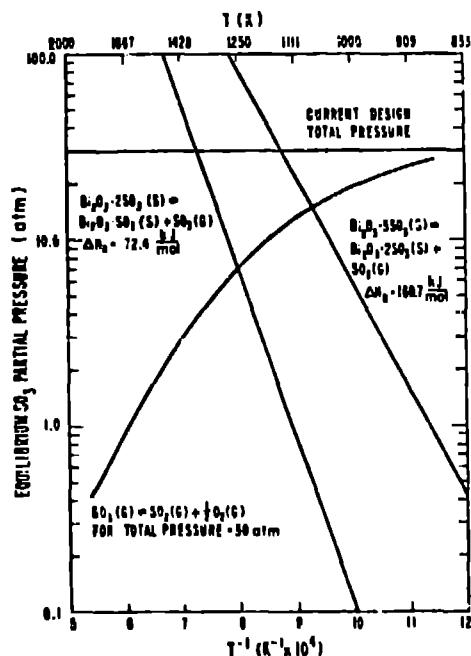


Fig. 3. Equilibrium Data for Bismuth Sulfate and Bismuth Oxysulfate Decomposition.

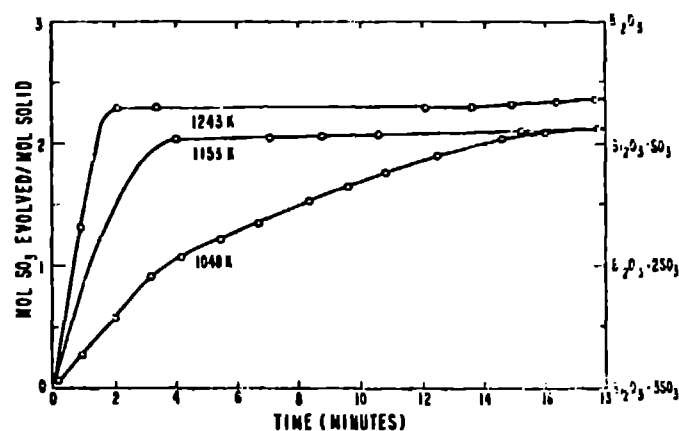


Fig. 4. Kinetics of Bismuth Sulfate Decomposition.

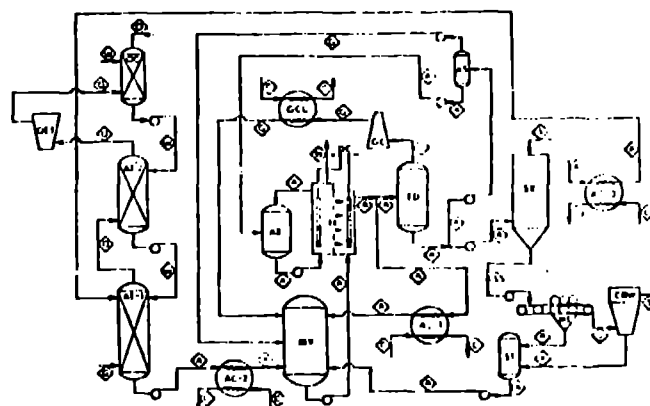


Fig. 5. Low-Temperature Portion Flowsheet - LASL Bismuth Sulfate Cycle

EL: Electrolyzer; AR: Acid reservoir; MV: Mixing vessel; AC-1, AC-2, AC-3: Acid coolers; SR: Solids reactor; FD: Flash drum; AT-1, AT-2: SO₂ absorption towers; ST: Surge Tank; ME: Mechanical expression rollers; CDW: Dewatering centrifuge; OET: Oxygen expansion turbine; OC: Oxygen cleanup tower; GCC: Gas cooler-condenser; GC: Gas compressor; AS: Acid separator; A: Aqueous sulfuric acid with and without SO₂; G: Sulfur dioxide containing gas; O: Predominately oxygen gas; W: Predominately water; C: Cooling water; S: Solids;

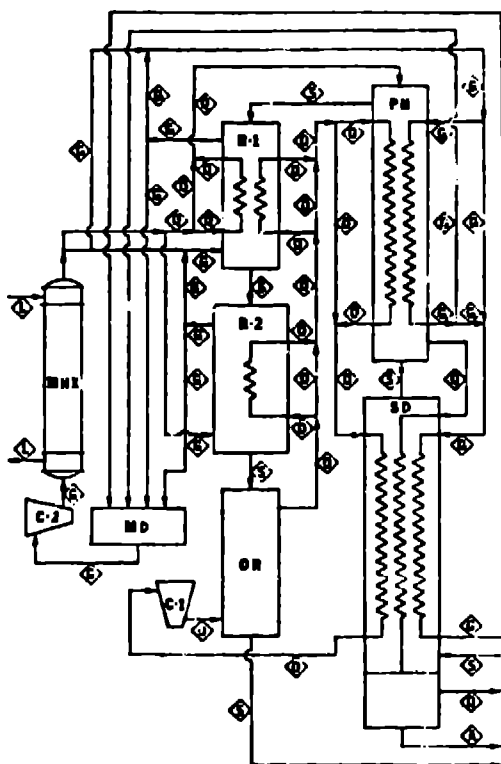


Fig. 6. High-Temperature Portion Flowsheet - LASL Bismuth Sulfate Cycle.

- L: Lithium stream, Q : $\text{SO}_3/\text{SO}_2/\text{O}_2$ gas quench stream.
A: Aqueous sulfuric acid stream, G: $\text{SO}_3/\text{SO}_2/\text{O}_2$ gas stream,
S: Bismuth oxysulfate solids stream (incl. occluded aq. acid),
O: Oxygen heat recuperation stream.
C-1,2: Compressors, MHX: Main heat exchanger, SD: Slurry drier,
PH: Solids preheater, R-1,2: Solids decomposition reactors,
OR: Direct contact oxygen heat recuperator, MD: Mixing drum.

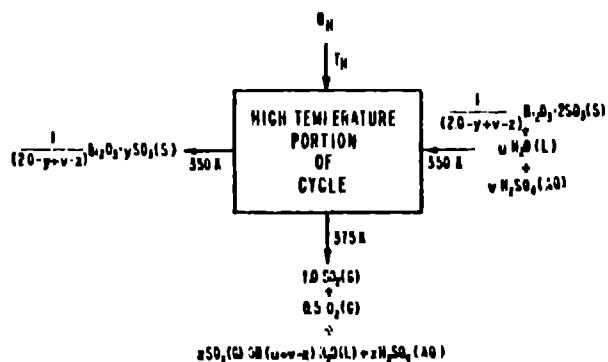


Fig. 7. High-Temperature Portion Energy Balance

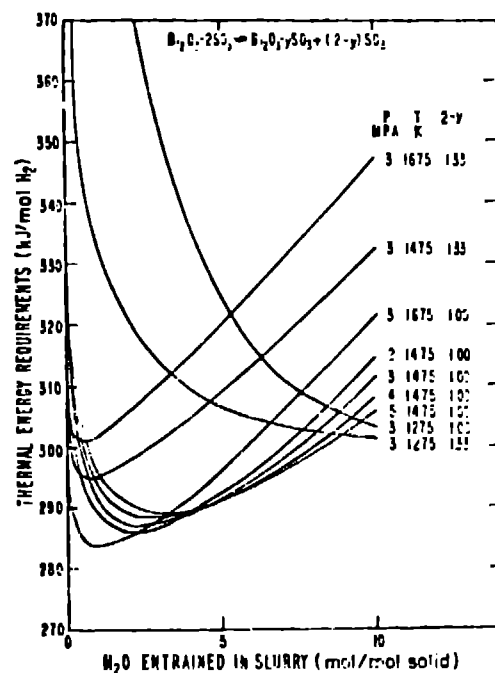


Fig. 8. Parametric Analysis of High-Temperature Portion of the Cycle.

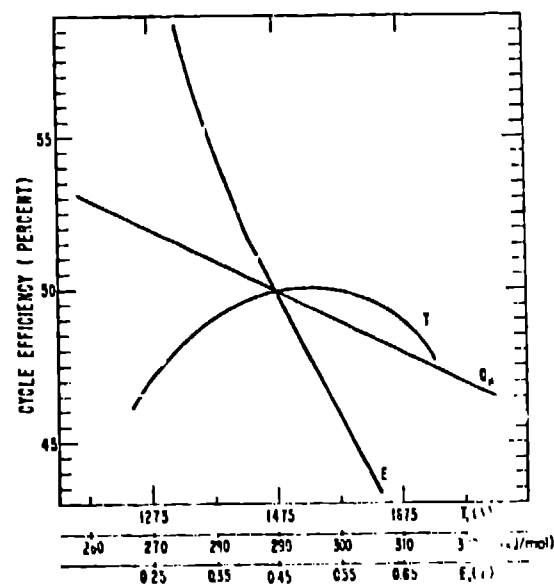


Fig. 9. Cycle Efficiency Parametric Analysis.